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PHYSICAL PROPERTIES AND THE STRUCTURE OF ALCOHOLIC LITHIUM CHLORIDE SOLUTIONS

By

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We have previously studied the physical properties and structure of pure liquids and in particular the character of intermolecular interaction found in such liquids (1, 2, 3, 4, 5). These studies allowed us to investigate in detail the intermolecular properties of liquids and solutions, as well as other physical characteristics of liquid state. In this article the results of studies pertaining to alcoholic solutions of lithium chloride are briefly reported.

Alcohols possess a similar molecular structure (6,7,8). Stewart (9) has investigated the X-ray scattering in solutions of lithium chloride in alcohols. He showed that with the increase in concentration of lithium chloride in an alcohol the X-ray diffraction patterns which are obtained on such concentrated solutions resemble the X-ray diffraction patterns of the solid lithium chloride-alcohol solutions.

We have carried out investigations pertaining to viscosity, density and critical parameters of alcoholic solutions of lithium chloride.

The solubility data pertaining to these solutions were either obtained in this laboratory or were obtained from the available literature. The solubility of lithium chloride in alcohols at temperatures somewhat higher than room temperature, passes through a maximum and with further rise in temperature the solubility generally decreases, reaching a minimum value at critical point of a saturated solution. The solubility of lithium chloride in methyl (M), ethyl (E), propyl (P) and butyl (B) alcohols are shown in Figure 1. The dotted lines indicate solubilities, and the solid lines indicate the LiCl concentration as a function of critical temperature for (E), propyl (P) and butyl (B) alcohols.

Figure 1 actually depicts solubility of lithium chloride in alcohols in a broad temperature range including the critical temperature region. The sloping (inclined) portions of concentration curves correspond to the unsaturated solutions, while the vertical portions to the saturated solutions, in presence of pure glass lithium chloride.

The precipitation rate of lithium chloride solids from the alcoholic solutions, kept in a motionless ampule, was found to increase and to decrease a maximum the closer the system was made to approach the critical point. It can be seen from Figure 1 that the higher is the critical temperature of solution the lower is (at all temperatures) the solubility of lithium chloride and the narrower is the concentration region of the unsaturated solutions which correspond to the critical region. These facts allow us to generalize that solubility is closely related to critical qualities of solutions. We have studied the density of lithium chloride solutions in ethyl, propyl and butyl alcohols in the 10-100°C temperature range. The magnitude of density polytherms of lithium chloride solutions in alcohol is greater the higher is the concentration of lithium chloride in the alcohol. The critical temperature of which exceeds the critical temperature of the solvent.

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The comparison of calculated values of apparent molecular volume of lithium chloride for given densities of solution and for pure solvent show these values to be smaller in the solutions. This decrease in apparent volume is a direct function with respect to increase in temperature and an inverse function with respect to increase in the salt concentration. Thus, for example, the apparent molecular volume of lithium chloride in a 1% solution in propyl alcohol at 72.5°C was calculated to be 18 cm³. With the increase in the critical temperature of the solution the magnitude of this decrease in the apparent molecular volume of lithium chloride was found to decrease.

The viscosity coefficients of lithium chloride solutions in methyl, ethyl, normal propyl and normal butyl alcohols were determined in the 50-100°C temperature range. In this temperature interval, the dependence of viscosity η on temperature is described by a simple exponential expression:

$$\eta = A \exp \frac{B}{T}$$

where A and B are coefficients which depend only on concentration and nature of the solvent. The viscosity polytherms of lithium chloride solutions in alcohols are shown in Figure 2. Also is shown graphically the functional relationship between η and $1/T$ for these solutions. The η - T curves which show continuous changes in solutions of lithium chloride in alcohol exhibit breaks when extended to temperatures approaching the critical region in which the presence of solid phase lithium chloride is evident.

In Figure 3 is shown graphically the relationship between concentration of LiCl solutions in alcohol and energy of activation (B) of the viscous flow. It can be seen that the values of the energy of activation of the viscous flow increase with concentration of lithium chloride in alcohol. For any concentration of lithium chloride in alcohol the values of B increase (while the values of A decrease) with the increase in the value of critical temperature of the alcohol. The study of the relationship of solution concentration and energy of activation of the viscous flow may be augmented by the knowledge of the nature of the molecular interaction as well as molecular structure of solutions.

Note worthy of attention is the fact that coefficients B of viscosity of lithium chloride in alcohols, concentrations of which correspond to solubility curves, for all the alcohols, are in the same order of magnitude as the values of B for molten lithium chloride. The same generalization can be made for values of coefficient A.

In Figure 4 we show the viscosity isotherms of alcoholic lithium chloride solutions at 50° and at 100°C. At any temperature and at any concentration the viscosity of solution is greater the greater is the critical temperature of the solvent.

The investigations, in the wide temperature range, of density, viscosity and solubility with a concurrent determination of critical parameters of solutions of lithium chloride allows to broaden and to extend the previously obtained information on physical properties and molecular character of solutions of other electrolytes.

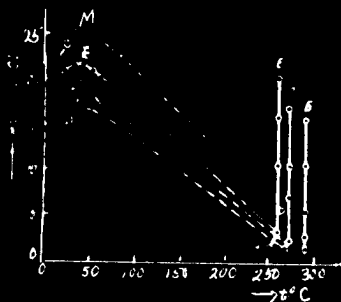


Figure 1. Solubility curves and concentration dependence on critical temperature of alcoholic solutions of lithium chloride. (Vertical axis: mol % LiCl)

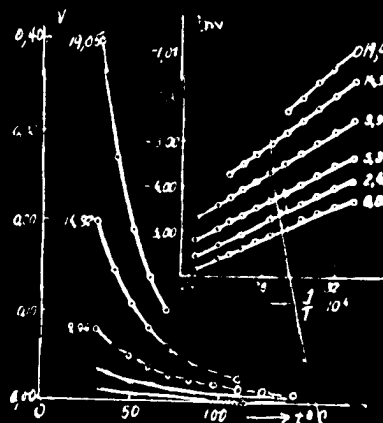


Figure 2. Viscosity polymers for ethyl alcohol solutions of lithium chloride. (Functional relationship $\ln \eta$ vs $1/T$ shown on the right. Numerical values next to curves represent mol % concentration of lithium chloride.)

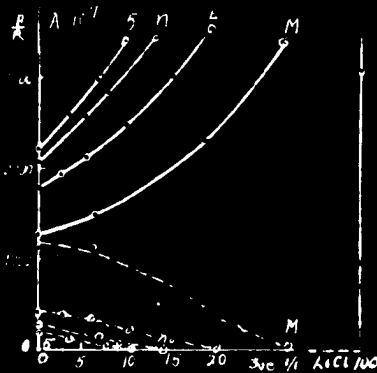


Figure 3. Concentration of activation of viscous flow (coefficient B - solid line) and of the pre-exponential factor (A - dotted line) of solutions of lithium chloride in methyl (M), ethyl (E), propyl (P) and butyl (B) alcohols.

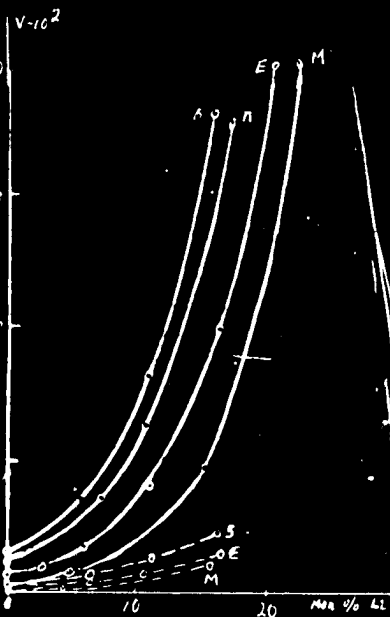


Figure 4. Viscosity isotherms for solutions of lithium chloride in methyl (M), ethyl (E), propyl (P) and butyl (B) alcohols at 30°C (solid lines) and at 120°C (Dotted lines).

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